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Changes in hydrocarbon content of heavy oil during hydrothermal process with nickel, cobalt, and iron carboxylates

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A B S T R A C T

We conducted autoclave modeling experiments to study the process of upgrading heavy oil in the reservoir conditions and used carboxylates of transition metals (Ni, Co, Fe) as catalyst precursors. The process was carried out at temperatures of 250, 300, and 350 °C in the presence of a naphthenoaromatic hydrogen donor. We found that significant content changes of oil occur at temperatures of 300 and 350 °C accompanied by an increase of light fractions and a decrease of high molecular weight hydrocarbons. We studied the hydrocarbon composition of the initial oil and the products of the hydrothermal process as well as tetralin (proton donor) transformations to determine the patterns of influence of the process conditions and catalyst precursors.

1. Introduction

The depletion of traditional oil reserves and increasing energy consumption motivate interest of oil companies in recovery of heavy crude oil and natural bitumen, which gradually become very important resources for stabilizing and enhancing oil production. According to different estimates by geologists, total reserves of heavy crude oil and natural bitumen range from 250 billion to 1 trillion tons, and are mainly located in the USA, Canada and Venezuela. As for Russia according to foreign sources, balance reserves of heavy oil and bitumen are from 47 to 55 billion tons to 214 billion tons (Muslimov, 2014). More than 60% of the heavy crude oil reserves are concentrated in the Volga-Ural basin, an area of more than 700 thousand km^2 and is located on the territory of several republics, include Republic of Tatarstan. One of the developed heavy oil fields in the Republic of Tatarstan is the Ashalchinskoye field. As of 2016, the main technology of oil production is steam gravity drainage. Combustion, steam injection in mixture with solvents, catalytic upgrading and various modifications thereof are considered among the potential methods of heavy oil extraction.

For the last few years, interest in hydrothermolysis (aquathermolysis) of heavy crude oil and natural bitumen has increased (Song et al., 2009; Kapadia et al., 2013; Hassanzadeh et al., 2016; 2017). Thermal transformations of heteroatomic compounds in a water vapor medium and in supercritical water are studied with the proceeding reaction of hydrogenation, hydrogenolysis, desulfuration (Liu, 2011; Antipenko et al., 2012; Lysogorskii and Aminova, 2015; Guo et al., 2017; Fedyaeva et al., 2017).

But, for the first time this researches was initiated by Clark and Hyne (Clark et al., 1983; 1984). They investigated thiophene and tetrahydrothiophene as models to study the reactivity of organosulfurs. With the same purpose Kartrizky, Siskin investigated different N-, O-, S-containing compounds (Siskin et al., 1990a,b; Katritzky et al., 1990). It should be mentioned that the decomposition of heterocompounds in realistic aquathermolysis process of heavy oil comes much more complicate rather than that in an ideal model compound system. Due to the fact that oil is a complex dispersion system (Sofieva, 2004) some reactions may come not so fast and efficiently as they do during pure compounds. Thus to reduce the activity energy of the reaction and control the process different catalyst are used.

Catalytic aquathermolysis is a promising technology for upgrading heavy oil in the reservoir conditions. The synthesis of inexpensive, efficient and universal catalysts, as well as understanding the mechanism of their action are essential for reducing heavy oil viscosity and for intensifying its production. Since the birth of the idea of catalytic oil aquathermolysis (Hyne et al., 1982; Weissman et al., 1996; Moore et al., 1999), numerous attempts have been made to study the mechanisms of their action and to develop corresponding catalysts (Wang et al., 2010; Liu, 2011; Ng and Milad, 2000; Kapadia et al., 2015; Xu et al., 2012;

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